Synthesis and Structural Features of a Series of κ^3SNS Pincer Complexes of Group 10 Metals σ-Bonded to Centered Pyrrolate Unit

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N-Metalation of *N*,*N*′-dibenzyl-1*H*-pyrrole-2,5-dicarbothioamide afforded new pincer complexes of group 10 metals with κ^3SNS-type coordination. Molecular structures of the complexes were characterized by X-ray crystallography.

Pincer complexes of group 10 metals have recently attracted much attention in catalysis and material science.[1] Such complexes with two five-membered metallacycle rings and a metal–C(phenyl) σ bond ((a) in Chart 1) have actively been studied. These pincer complexes are generally formed by the ortho,ortho-cyclometalation reaction of the starting ligand by the transition metals or transmetalation of the corresponding lithiated ligand. The complexes are stabilized by the ancillary chelating donor atom E.

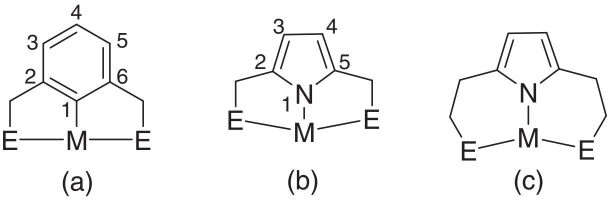
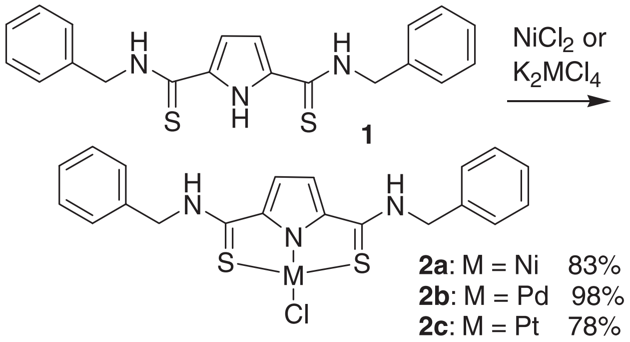


Chart 1. Pincer complexes: E = chelating donor atom.

Pyrrole is a building block of porphyrin, phthalocyanine, and related ligands.[2] N-Metalation of pyrrole to give the pincer type complex (b) in Chart 1 is intriguing because, in contrast to the case of the complex (a), the 2- and 5-positions in the complex (b) is connected with a π-conjugated system which would render interesting electronic properties to the complex. However, examples of such square-planar pincer complexes containing the centered pyrrole ring have been limited.[3–5] For group 10 metal complexes, only a few κ^3ENE-type pincer palladium complexes with the centered pyrrolate unit have been reported. The isolated κ^3ENE–Pd pincer complexes, so far reported, have the structure (c) depicted in Chart 1, with two six-membered rings.[4] Preparation of κ^3ENE-type pincer complexes of Ni and Pt has no precedent.

Preparation of phenyl-bis(thioamide)-based κ^3SCS pincer Pd and Pt complexes of the type (a) shown in Chart 1 has previously been reported.[6] In the previous studies, it was found that the phenyl-bis(thioamide) pincer ligands served as a flexible and good ligand for various pincer complexes. Nonoyama et al. also reported that cyclopalladation of N–H bond in pyrrole could occur for *N*,*N*-dimethyl-1*H*-pyrrole-2-carbothioamide.[7] On these bases, the present work is concerned with cyclometalation of the following pyrrole derivative **1** with two thioamide side groups to form a new series of the κ^3ENE-type pincer complexes of Ni, Pd, and Pt. The newly prepared complexes have the type (b) structure exhibited in Chart 1. We here report preparation and the molecular structures of the κ^3SNS pincer complexes.



Scheme 1.

The pincer ligand **1** was prepared by the Willgerodt–Kindler reaction of pyrrole-2,5-dicarboxyaldehyde with benzylamine in the presence of sulfur according to the previous reports.[6–8] Reaction of **1** with $NiCl_2\cdot6H_2O$ readily led to deprotonation of the pyrrole nitrogen even in the absence of base at room temperature, and afforded the κ^3SNS pincer Ni complex (Ni(**1**-H)Cl, **2a**). Similar cyclometalation of **1** with K_2MCl_4 (M = Pd and Pt) yielded the corresponding κ^3SNS pincer complexes (M(**1**-H)Cl, **2b**: M = Pd; **2c**: M = Pt) in good yields (Scheme 1).[8]

The complexes **2a**–**2c** were fairly stable to air and water, and showed good solubility in organic solvents such as methanol, acetone, THF, and DMSO. Structures of **2a**–**2c** were confirmed by NMR, IR, and FAB-MS spectroscopy and elemental analysis.[8] In the ^{1}H NMR spectra of **2a**–**2c**, the NH signal of pyrrole ring disappeared, and a downfield shift (by 0.43–1.17 ppm) of the NH signal of the thioamide groups was observed. The ν(C–N) IR peak of **1** (1541 cm^{-1}) shifted to a higher frequency (1568, 1554, and 1563 cm^{-1} for **2a**, **2b**, and **2c**, respectively) according to the *S*-coordination of the group.[6c,6d,7,9]

The ORTEP drawing of **2b** is presented in Figure 1.[10] The complex **2b** has a κ^3SNS-type coordination with a distorted square-planar geometry. The S–Pd–S bond angle is smaller and the Pd–S bond lengths are larger than those observed with related phenyl-bis(thioamide)-based κ^3SCS-type pincer palladium complexes (cf. Table S1 in Electronic Supporting Information).[6] The pyrrolate nitrogen atom is σ-bonded to palladium with a Pd–N bond length of 1.932(3) Å, which is comparable to that observed for the reported κ^3NNN pincer Pd complexes of the type (c) in Chart 1,[4a] whereas the centered pyrrole ring is slightly tilted from the planes spanned by the four donor atoms with dihedral angle of 1.1°. The C–C and C–N bond lengths of the centered pyrrole ring are reminiscent of those observed for Pd(II)–porphyrin complexes,[11] and the pyrrole ring is almost co-planar to the thioamide units as revealed by torsion angles of C2–C1–C5–N1 and C2–C1–C5–S1 in Figure 1. It indicates

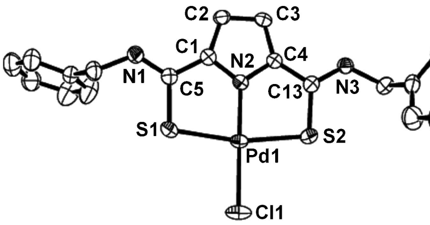


Figure 1. ORTEP view of **2b** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and a solvated acetonitrile molecule are omitted for simplicity. Selected bond lengths (Å), angles (°), and torsion angles (°): Pd(1)–Cl(1) = 2.3173(12), Pd(1)–S(1) = 2.3238(10), Pd(1)–S(2) = 2.3256(10), Pd(1)–N(2) = 1.932(3), Cl(1)–Pd(1)–N(2) = 179.16(8), S(1)–Pd(1)–S(2) = 166.78(4), C(2)–C(1)–C(5)–N(1) = 178.8(3), C(2)–C(1)–C(5)–S(1) = 179.4(3).

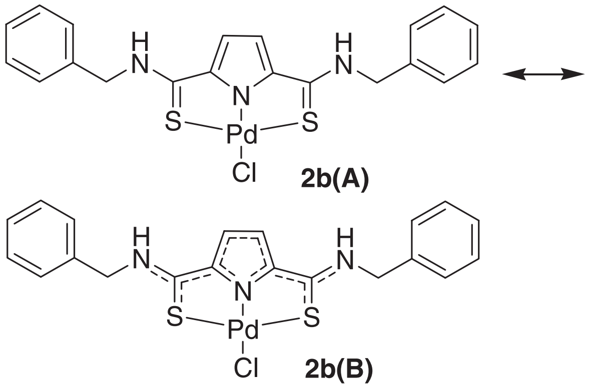


Chart 2. Delocallization of electron in **2b**.

the presence of an exocyclic double bond character in the complex. The C=S bond lengths are somewhat longer while the C–C(S) and the C(S)–N bond lengths are shorter than those observed with related phenyl-bis(thioamide)-based κ^3SCS-type pincer palladium complexes (cf. Table S1).[6] The structural feature suggests that cyclometalation of **1** enhances delocalization of electron in the centered pyrrole ring and the thioamide group (**2b(B)** in Chart 2). Similar delocalization of electron in the pincer ligand was suggested for κ^3SPS pincer complexes containing a phosphinine-centered ligand with two phosphine sulfide groups.[12]

Interestingly, the X-ray crystallographic data of **2b** reveals that an intermolecular N–H···Cl hydrogen bond of **2b** leads to formation of a linear-chain network structure along the *c* axis in the solid state as depicted in Figure 2. **2b** contains a CH_3CN molecule and CH_3CN links with the NH hydrogen of the thioamide group in another wing of the ligand via an N–H···N≡C hydrogen bond.

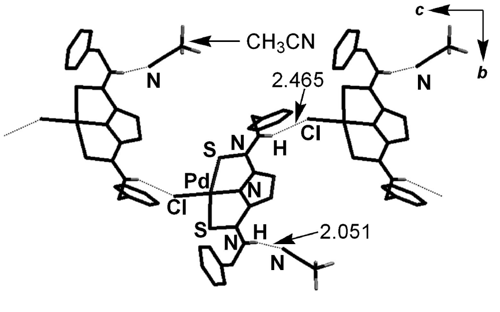


Figure 2. View of **2b** from the *a* axis. The N–H···Cl and N–H···N hydrogen-bonding distances are given in Å.

The Ni complex **2a** has a molecular structure similar to that of the Pd complex.[8,10] Determination of the Pt complex **2c** crystallographical molecular structure has not been successful.

As described above, cyclometalation of **1** including N-metalation of pyrrole ring readily afforded the κ^3SNS pincer complexes even in the absence of base. This is the first example of the square-planar pincer complexes of group 10 metals having centered pyrrolate unit with two five-membered metallacycles.

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10 Crystal data for **2a**•CH_3CN: $C_{22}H_{21}ClN_4S_2Ni$, M_r 547.41, monoclinic, $P2_1/c$, $a = 8.6060(13)$, $b = 16.319(2)$, $c = 15.875(2)$ Å, $\beta = 98.0019(8)°$, $V = 2207.9(6)$ Å^3, $Z = 4$, $D_{calcd} = 1.503$ g/cm^3, Observed reflections 3020 ($I > 2\sigma(I)$), $R_1 = 0.028$, $wR_2 = 0.029$, $S = 1.06$. For **2b**•CH_3CN: $C_{22}H_{21}ClN_4S_2Pd$, M_r 499.71, monoclinic, $P2_1/c$, $a = 8.896(3)$, $b = 16.151(5)$, $c = 15.829(5)$ Å, $\beta = 100.089(4)°$, $V = 2239.2(12)$ Å^3, $Z = 4$, $D_{calcd} = 1.624$ g/cm^3, Observed reflections 3734 ($I > 2\sigma(I)$), $R_1 = 0.037$, $wR_2 = 0.044$, $S = 1.00$. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC-297470 (**2b**•CH_3CN) and CCDC-297471 (**2a**•CH_3CN). Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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